

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
30 November 2000 (30.11.2000)

PCT

(10) International Publication Number
WO 00/71337 A1

(51) International Patent Classification⁷: B32B 25/04, 25/12, 27/08, 27/38, C08G 59/00

(74) Agent: MURPHY, Glenn, E., J.; Henkel Corporation, Suite 200, 2500 Renaissance Boulevard, Gulph Mills, PA 19406 (US).

(21) International Application Number: PCT/US00/14528

(22) International Filing Date: 26 May 2000 (26.05.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/136,048 26 May 1999 (26.05.1999) US
60/146,001 26 May 1999 (26.05.1999) US

(71) Applicant: HENKEL CORPORATION [US/US]; Suite 200, 2500 Renaissance Boulevard, Gulph Mills, PA 19406 (US).

(72) Inventors: AGARWAL, Rajat, K.; 34271 Coastal Drive, Sterling Heights, MI 48310 (US). Bammel, Brian, D.; 447 Parkland Drive, Rochester Hills, MI 48307 (US). FRISTAD, William, E.; 3724 New Castle Drive, Rochester Hills, MI 48306 (US). ROSSIER, Gregg, W.; 2525 Foxcliff N., Martinsville, IN 46151 (US). SIEBERT, Elizabeth, J.; 1755 Butterfield, Troy, MI 48084 (US). YANG, Zhiqi; 2395 Sweet Drive, Troy, MI 48098 (US).

(81) Designated States (national): AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— With international search report.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 00/71337 A1

(54) Title: AUTODEPOSITION COATINGS AND PROCESS THEREFOR

(57) Abstract: Autodeposited coatings useful for protecting metal surfaces and in the production of rubber-to-metal composites are obtained by curing polymers based on epoxy resins which are adhered to the metal surfaces. One or more epoxy resins, such as for example, the combination of a diglycidyl ether of bisphenol A and a flexibilizing epoxy resin, may be prereacted to form a polymer of higher average molecular weight than the starting epoxy resins. Said polymer may then be emulsified in water, with the resulting emulsion being used in an autodeposition bath composition.

AUTODEPOSITION COATINGS AND PROCESS THEREFOR

5 FIELD OF THE INVENTION

This invention relates to coatings for metallic substrates which are based on epoxy resins as well as to methods of preparing emulsions or dispersions suitable for forming such coatings through autodeposition.

10 DISCUSSION OF THE RELATED ART

Over the last few decades, various water-based coatings for metallic surfaces have been developed which are commonly referred to in the field as autodeposition coatings. Such coatings utilize an emulsion or dispersion of a resin capable of forming a protective coating when cured.

15 The coating typically is applied by immersing the metallic surface in a bath containing the resin emulsion or dispersion, acid, and an oxidizing agent to form an adherent coating that is initially wet. The thickness of the coating can be affected, for example, by such factors as total solids, pH and oxidant concentration. Further, the coating thickness is a function of the immersion time. The initial wet coating is sufficiently adherent to remain attached to the surface on which it is formed against the influence of normal gravity and, if desired, can be rinsed before being cured (i.e., converted to a dry, solid and even more adherent coating) by heating.

20 A number of different resins have been proposed for use in autodeposition coatings, as described, for example, in U.S. Patent Numbers 3,063,877;

3,585,084; 3,592,699; 3,647,567; 3,791,431; 4,030,945; 4,186,226; 3,795,546; 4,636,265; 4,636,264; and 4,800,106, each of which is incorporated herein by reference in its entirety.

Epoxy resin-based autodeposition coating systems are described in 5 U.S. Patent Numbers 4,233,197; 4,180,603; 4,289,826; and 5,500,460 and in International Publication Number WO 97/07163 (corresponding to U.S. Serial Number 60/002,782, filed August 16, 1995), the teachings of each of which are incorporated herein by reference in their entirety. However, 10 it is believed that none of the autodeposition coatings currently being supplied on a commercial basis utilize epoxy resins. The epoxy resin-based autodeposition coatings developed to date all apparently have one or more shortcomings which have limited their usefulness relative to other coatings such as those based on polyvinylidene chloride or acrylic resins. 15 In particular, inconsistent coating appearance and quality have been a major disadvantage for epoxy resin-based autodeposition coatings.

SUMMARY OF THE INVENTION

This invention provides a metallic substrate having a coating adhered thereto, said coating being obtained by autodepositing a polymer containing 20 moieties derived from at least one epoxy resin which is a glycidyl ether of a first polyhydric phenol and at least one flexibilizing epoxy resin on said metallic substrate and curing said polymer.

This invention also provides a composite comprised of the

aforementioned coated metallic substrate, a rubber, and an adhesive bonding said metallic substrate to said rubber.

Additionally, this invention provides a method of making an aqueous dispersion suitable for use in forming an autodeposited surface coating, said method comprising

- 5 a) contacting at least one epoxy resin and at least one chain extender containing at least two epoxy-reactive groups such as hydroxyl, carboxylic acid, carboxylic acid anhydride, and combinations thereof for a time and at a temperature effective to accomplish reaction of said epoxy resin and chain extender to form a polymer having an increased molecular weight as compared to the epoxy resin;
- 10 b) emulsifying a solution of the polymer (and, preferably, at least one cross-linker capable of reacting with functional groups present in the polymer) in an organic solvent with water in the presence of an emulsifier to form an organic solvent-containing intermediate emulsion; and
- 15 c) removing the organic solvent from the organic solvent-containing intermediate emulsion to form the aqueous dispersion.

This invention also provides an autodeposition bath composition comprising (a) at least one of the aforescribed polymers, (b) at least one emulsifier, (c) at least one cross-linker, (d) at least one accelerator component such as acid, oxidizing agent and/or complexing agents, (e) optionally, at least one colorant, (f) optionally, at least one filler, (g)

optionally, at least one coalescing agent, and (h) water.

Also furnished by this invention is a method of coating a metallic substrate comprising the steps of contacting said metallic substrate with the aforescribed autodeposition bath composition for a sufficient time to cause the formation of a film of the polymer on a surface of the metallic substrate, separating the metallic substrate from contact with the autodeposition bath composition, rinsing the metallic substrate, and heating the metallic substrate to cure the film of the polymer adhered to said surface.

5

10 DETAILED DESCRIPTION OF THE INVENTION

The present invention is capable of providing autodeposited coatings on metallic substrates which have improved resistance against corrosion and moisture, improved edge coverage, flow, levelling and film formation properties and reduced VOC (volatile organic compound) levels as compared 15 to previously known autodeposition coatings.

One or more epoxy resins are utilized in the present invention. Epoxy resins are well known substances and are described, for example, in the chapter entitled "Epoxy Resins" in Volume 6 of The Encyclopedia of Polymer Science and Engineering (Second Edition). Preferably, at 20 least one of the epoxy resins is a glycidyl ether of a polyhydric phenol.

Such epoxy resins preferably contain approximately two epoxide groups per molecule. The polyhydric phenol may be any compound containing one or more aromatic rings and two or more hydroxy

5

groups such as bisphenol A (a particularly preferred species of polyhydric phenol), bisphenol F, bisphenol AD, catechol, resorcinol, and the like. It will generally be desirable to utilize epoxy resins of the type which have relatively low epoxide equivalent molecular weights (e.g., about 75 to about 300) and/or which are liquid at ambient temperatures.

10

In one particularly desirable embodiment, at least one diglycidyl ether of bisphenol A having an epoxide equivalent weight of about 150 to about 300 is used in combination with at least one flexibilizing epoxy resin. The use of a flexibilizing epoxy resin has been found to reduce the extent of crazing observed in the coating under low humidity coating conditions.

15

Suitable flexibilizing epoxy resins include those compounds containing at least one epoxide group per molecule and one or more groups capable of increasing the flexibility of the polymer such as, for example, long aliphatic chains (e.g., polymethylene chains corresponding, for example, to the structure $-(CH_2)_n-$ wherein n is preferably >3, more preferably, >6; the polymethylene chains can be in the backbone of the flexibilizing epoxy resin and/or pendent thereto), polyester chains (especially those formed by condensation of aliphatic diacids and glycols or glycol oligomers),

20

polyoxyalkylene chains (e.g., polyether chains corresponding to the structure $-((CH_2)_n-CHR-O)_m-$, where n is 0-3, m is 2 or greater, and R is H or alkyl), and the like. A particularly preferred flexibilizing epoxy resin is a difunctional epoxy derived from cardanol (a phenol substituted with a long chain

unsaturated hydrocarbon group which is obtained from cashew nut oil) having an epoxy equivalent weight of about 350; such a material is available from the Cardolite Corporation of Newark, New Jersey, under the trademark CARDOLITE NC-514. CARDOLITE NC-513, which is believed to be 5 expoxidized cardanol having a single epoxy group per molecule, and CARDOLITE NC-551 have also been found to be useful in the present invention. The relative ratio of bisphenol A diglycidyl ether to flexibilizing epoxy resin can be varied considerably depending upon the individual components selected and the properties desired in the final autodeposition 10 coating. Typically, however, it will be desirable to use less flexibilizing epoxy resin than bisphenol A diglycidyl ether on an equivalents basis. For example, the ratio of flexibilizing epoxy resin:bisphenol A diglycidyl ether may suitably be from about 0.05 to about 0.40 (as calculated from the epoxide equivalent 15 weight of each component). Typically, the flexibilizing segments will comprise from about 1 to about 25 % by weight of the polymer.

Other methods of introducing flexibilizing segments such as polymethylene or polyoxyalkylene into the polymer may also be employed. For example, the chain extender discussed in more detail below may contain such moieties, either in the backbone of the chain extender or 20 pendent thereto. Alternatively, some or all of the epoxy groups of the polymer could be reacted with a compound containing one or more flexibilizing segments (e.g., a long chain fatty acid such as pelargonic acid or a monoether of an aliphatic polyether diol). The hydroxy groups of the

polymer could also be derivatized with compounds containing flexibilizing segments (for example, the hydroxy groups could be esterified with a long chain fatty acid).

A chain extender is utilized to react individual epoxy resin molecules through their epoxy groups so as to form a polymer which is higher in average molecular weight than the starting epoxy resin(s). In one embodiment of the invention, the average molecular weight is increased at least 100%, more preferably at least about 200%, relative to the initial average molecular weight of the starting epoxy resin or combination of epoxy resins. The chain extender thus should contain at least two functional groups capable of reacting with said epoxy group such as, for example, hydroxy, carboxylic acid, carboxylic acid anhydride or the like. In one embodiment of the invention, the chain extender is a polyhydric phenol such as bisphenol A. Alkoxylated polyhydric phenols such as SYNFA 8009 (available from Milliken Chemical) may also be used as chain extenders. Suitable chain extenders additionally include dicarboxylic acids such as adipic acid.

In one embodiment of the invention a diglycidyl ether of a polyhydric phenol such as bisphenol A is used in combination with a chain extender which contains one or more flexibilizing segments such as polymethylene, polyester or polyoxyalkylene segments. For example, a polyether polyol such as polypropylene glycol, polyester polyol (hydroxy and/or carboxylic acid terminated), dimer fatty acid, long chain dicarboxylic acid (e.g.,

decanedioic acid), long chain diol (e.g., 1,12-decanediol), or the like could be used.

The stoichiometry of chain extender(s) to epoxy resin(s) is adjusted depending upon the degree of condensation (i.e., chain extension) desired in forming the polymer. Typically, however, the amount of epoxy resin(s) is kept in slight to moderate excess relative to the amount of chain extender(s).

For example, the equivalents of epoxy groups in the epoxy resin(s) may be about 5% to about 50% greater than the equivalents of active hydrogen groups in the chain extender(s). The polymer formed thus will contain unreacted epoxy groups (i.e., the polymer will be epoxy-functionalized).

Typically, the polymer will also contain hydroxy (-OH) groups, which may be present in the initial epoxy resin(s) or which may be formed as a consequence of the reaction between the chain extender and the epoxy groups of the epoxy resin.

The epoxy resin(s) and chain extender(s) are reacted for a time and at a temperature effective to cause the desired degree of condensation and chain extension. In one embodiment of the invention, for example, the epoxide equivalent weight of the polymer formed will be in the range of at least about 1000, preferably at least about 1500, as compared to epoxide equivalent weights for the starting epoxy resin reactant(s) of from about 75 to about 500. Such conditions will vary depending upon the relative reactivity of the components and other factors, but may be optimized without undue experimentation. Catalysts capable of accelerating the desired epoxy group

reaction with the chain extender such as phosphines, amines and other basic substances may be utilized if so desired in order to reduce the reaction time and/or temperature required. The reaction may be carried out in the presence of a solvent capable of dissolving both the epoxy resin(s) and the chain extender(s) such as, for example, an inert organic solvent (e.g., aromatic hydrocarbons, ketones).

In one desirable embodiment of the invention, the polymer derived from the epoxy resin(s) and chain extender(s) is prepared prior to forming an emulsion of said polymer in water. A solution of the polymer in one or more organic solvents is emulsified with water in the presence of one or more emulsifiers to form an organic solvent-containing intermediate emulsion. The organic solvent(s) used in said emulsification step may be the same as or different from the organic solvent(s) used when reacting the epoxy resin(s) and chain extender(s). Other desired components such as cross-linkers, coalescing agents, flow control additives (levelling agents), and the like may also be incorporated into the emulsion, either as components pre-dissolved in the organic (solvent) phase or added separately to the emulsion.

Suitable cross-linkers include molecules containing at least two functional groups such as amine, amide, imine, thiol, hydroxyl, carboxyl, and carboxylic acid anhydride that are capable of chemical addition reactions with the epoxy groups present in the polymer when heated to a temperature of at least 100°C as well as molecules containing at least two blocked isocyanate

groups. Each such isocyanate group is masked with a blocking group such as a ketoxime, urea (formed using an alcohol or phenol), uretdione, or group derived from the lactam of 6-aminohexanoic acid and/or benzotriazole, so that the blocked isocyanate group does not react at any appreciable rate at 5 room temperature with hydroxyl groups but does react rapidly with such groups after being unblocked by heating to a temperature of at least about 100°C. Suitable cross-linkers of these types are described, for example, in U.S. Patent Number 5,500,460 and WO 97/07163. The use of isophorone diisocyanate-based, epsilon-caprolactam blocked isocyanates as crosslinker, 10 such as the product sold by Huels under the trademark VESTAGON B1530, is particularly preferred. If a blocked isocyanate-type crosslinker is utilized, the ratio of blocked isocyanate groups to hydroxy groups (NCO:OH) typically will be in the range of about 0.05 to about 1.2, more preferably about 0.1 to about 0.5.

15 Generally, the presence of one or more coalescing agents in the autodeposition bath compositions of this invention will be desirable in order to optimize the properties of the cured coatings obtained therefrom. Coalescing agents, for example, help to minimize the blistering problems sometimes exhibited by autodeposited coatings. At the same time, however, 20 it will generally be desirable for environmental and economic reasons to limit the amount of coalescing agent utilized. In certain embodiments of the invention, it is possible to omit coalescing agent(s) altogether and yet still

obtain autodeposited coatings meeting all minimum criteria for commercial acceptance. The coalescing agent(s) are preferably selected from the group consisting of monoethers and monoesters of glycols. The glycols may be monomeric or oligomeric in structure. Illustrative coalescing agents include, 5 but are not limited to, propylene glycol mono-n-butyl ether, propylene glycol mono-phenol ether, and 2,2,4-trimethyl-1,3-pentanediol mono 2-methyl propionate.

The emulsifier(s) used may be any of the substances capable of stabilizing the emulsion of the polymer in water and preferably are anionic 10 surfactants such as sulfonates and sulfates. Preferred anionic surfactants are ether sulfates corresponding to the general formula $M^+ \cdot O-SO_2-O-(CH_2-CH_2-O)_p-R$ where M^+ is a monovalent cation or monovalent fraction of a cation of higher valence, preferably sodium or ammonium, p is a positive integer (preferably, equal to 2 or more), and R is an alkyl or alkyl aryl moiety 15 (preferably, an alkyl phenol moiety), preferably containing at least 8 but not more than 30 carbon atoms. The polymer is regarded as stably emulsified if no separation or segregation of the polymer phase that is perceptible with normal unaided human vision occurs during storage at 25 degrees C for at least 24 hours after preparation of the emulsion.

20 Suitable flow control additives or levelling agents include, for example, the acrylic (polyacrylate) substances known in the coatings art such as the products sold under the trademark MODAFLOW by Monsanto, as well as

other levelling agents such as BYK-310 (BYK-Chemie), PERENOL F-60 (Henkel), and FLUORAD FC-430 (3M).

Emulsification may be accomplished by any of the emulsification procedures known in the art. Preferably, however, the procedures described 5 in International Publication Number WO 97/07163 (corresponding to U.S. Patent Number 60/002,782, filed August 16, 1995) are followed. These procedures involve a two stage process in which a solution of the polymer in a suitable solvent such as an aromatic hydrocarbon (especially those containing 6 to 10 carbon atoms such as toluene) and/or an aliphatic ketone 10 (especially those containing 3 to 8 carbon atoms such as methyl isobutyl ketone) is emulsified into water to form a preliminary dispersion and the preliminary dispersion is subjected to at least one particle size refinement stage in which the preliminary dispersion is forced through a narrow aperture. The particle size distribution of the resulting emulsion preferably satisfies the 15 following criteria: (1) the mean light scattering particle size is at least about 100 but not more than about 300 nm; (2) no more than about 1.0% of the light scattering particles volume consists of particles with a diameter greater than about 450 nm; (3) no more than about 25% of the light scattering particles volume consists of particles with a diameter larger than about 300 20 nm; (4) no more than about 50% of the light scattering particles volume consists of particles with a diameter larger than about 275 nm; and (5) no more than about 75% of the light scattering particles volume consists of

particles with a diameter larger than about 250 nm.

Following emulsification, it will generally be desirable to remove any organic solvent(s) present by an appropriate means such as, for example, distillation. Where the polymer is a solid at 25 degrees C, solvent removal will normally result in the formation of a dispersion (i.e., solid particles of polymer dispersed in water). The temperature during distillation should be controlled in order to avoid premature curing or cross-linking of the polymer by the cross-linker. The distillation may be conducted under reduced pressure if the normal boiling point of the solvent to be removed is higher than the desired distillation temperature. The solvent removal conditions are also preferably selected such that the organic solvent(s), but not the coalescing agent(s), are separated from the emulsion. For this reason, it will be desirable to use a solvent which has a boiling point (or an azeotropic boiling point with water) which is lower than the boiling point(s) of the coalescing agent(s). Alternatively, the organic solvent component of the emulsion may be left in when the emulsion is used in an autodeposition coating process; any solvent remaining in the wet coating may be removed during the curing step.

To prepare a bath composition suitable for coating a metallic substrate by autodeposition, the aforescribed emulsion or dispersion is combined with an accelerator such as acid, oxidizing agent, and/or complexing agent which is capable of causing the dissolution of active

metals (e.g., iron) from the surface of the metallic substrate in contact with the bath composition. Preferably, the amount of accelerator present is sufficient to dissolve at least about 0.020 gram equivalent weight of metal ions per hour per square decimeter of contacted surface at a temperature of 5 20°C. Preferably, the accelerator(s) are utilized in a concentration effective to impart to the bath composition an oxidation-reduction potential that is at least 100 millivolts more oxidizing than a standard hydrogen electrode. Such accelerators are well-known in the autodeposition coating field and include, for example, hydrofluoric acid and its salts, fluorosilicic acid and its salts, 10 fluorotitanic acid and its salts, salts comprising ferric ions, acetic acid, phosphoric acid, sulfuric acid, nitric acid, hydrogen peroxide, peroxy acids, citric acid and its salts, and tartaric acid and its salts. The pH of the bath composition preferably is in the range of from about 2 to about 4.

The autodeposition bath composition may additionally contain, if 15 desired, pigment, filler, or other dispersed solid phase materials, dyes or other dissolved colorants, plasticizers as well as other of the components conventionally used in the autodeposition coating field. The crosslinkers and coalescing solvents previously mentioned may, of course, be combined with the emulsion or dispersion after it has been formed rather than during the 20 emulsification process, if so desired. The relative proportions and concentrations of the various components of the autodeposition bath composition may be the same as those set forth in WO97/07163.

5

The epoxy resin-devised polymers described herein may be used in combination with other autodeposition resins, including, for example, acrylic polymers such as those obtained by emulsion polymerization of alkyl, hydroxyalkyl and glycidyl acrylates and methacrylates, acrylic acid, methacrylic acid, acrylamides, and the like, either as homopolymers, copolymers, or copolymers with other monomers such as olefins, styrene, vinyl chloride, vinylidene chloride, and vinyl acetate.

10

15

A coating process according to this invention comprises the steps of contacting an object with an active metal surface with the aforescribed autodeposition bath composition for a sufficient time to cause the formation of a film of the polymer of a pre-determined thickness on the metal surface, separating the coated metal surface from contact with the autodeposition bath composition, rinsing the coated metal surface to remove at least some of the absorbed but otherwise unadhered components of the bath composition from the more adherent portion of the coating and heating the rinsed surface to form a final film. Without wishing to be bound by theory, it is believed that when the wet adherent coating is heated, the polymer and cross-linker present in the emulsion react to form a thermoset polymeric matrix.

20

Optionally, a reagent capable of causing additional desirable reactions in the coated film may be included in the rinse used after cessation of contact between the wet coated surface and the bulk of the autodeposition bath composition. Such a reagent may also be brought into contact with the

wet coated film after rinsing with water alone. Although the autodeposition bath compositions of the invention generally produce wet coated films that can be heated after simple rinsing with tap or deionized water to give good quality final films, the corrosion resistance of the cured coating may be 5 further improved by rinsing with an aqueous solution of an alkaline earth metal compound such as calcium nitrate as described in copending provisional application Serial Number 60/135,304, filed May 21, 1999 (Attorney's Docket Number M 6616), incorporated herein by reference in its entirety.

10 Preferably, contact between an active metal surface and the autodeposition bath compositions of this invention is for a time between about 0.5 and about 10 minutes, more preferably between about 1 and about 3 minutes. Contact preferably is long enough to produce a final film thickness of from about 15 to about 50 um. Final heating of the rinsed wet 15 coated and optionally post-treated polymer film is preferably at a temperature of from about 100°C to about 300°C, more preferably between about 130°C and 200°C, for a time of about 3 to about 60 minutes.

20 The cured coatings obtained by practice of this invention are useful as protective and decorative finishes on metal objects, but are also useful in the production of rubber-to-metal composites. Rubber-to-metal composites are of considerable importance in many branches of industry. The bond between rubber and metal is normally achieved with the use of one or more commonly two special thermosettable compositions that serve as cements

5

in joining the metal to the bulk rubber. To obtain the best adhesion, however, it is generally necessary to first treat the metal surface with a phosphating agent. Once the rubber is bonded to the phosphated metal, a final paint topcoat is normally applied so as to obtain a composite having a pleasing appearance.

The use of a pigmented autodeposited coating as a protective coating before bonding a rubber to a metal surface eliminates the need to phosphate the metal surface and to apply a paint topcoat after forming the rubber-to-metal composite, resulting in a simpler, more economical process.

10

The appearance of the autodeposited coating, which may still be visible on those areas of the metal surface not covered by the rubber, is quite satisfactory for many end-use applications in industry. The presence of the autodeposited coating on the exposed areas of the metal surface not covered by the rubber also provides the corrosion resistance normally required in such applications. Additionally, the adhesion of the rubber to the autodeposition coated metal surface is at least as good as the adhesion of the same rubber to a phosphated metal surface. Only one adhesive layer need be applied to create a strong and durable bond, thus resulting in further cost savings and lower VOC emulsions due to reduced adhesive usage.

15

Any of the rubbers (elastomers) known in the art may be utilized in such composites, such as, for example, natural rubber, nitrile rubber, styrene-butadiene rubber, butyl rubber, EPDM, diene rubber, and the like. Typically, the rubber will be vulcanizable rather than thermoplastic and will

thus contain one or more of the curatives (sulfur, peroxide), accelerators, fillers, pigments, waxes, plasticizers, extenders, or the like known in the art.

The adhesive used to join the rubber to the autodeposition coated metal surface may be any of the adhesives conventionally used to adhere rubber to untreated or treated metal surfaces. The use of adhesive formulations based on halogenated polymers such as chlorinated rubber is especially desirable, although other types of adhesives such as cyanoacrylates and epoxies may also be employed. Exemplary chlorinated rubbers include, but are not limited to, chlorinated polybutadiene, chlorinated 5 copolymers of butadiene and styrene, and mixtures of chlorinated rubbers or hypohalogenated rubbers and the like. The polychloroprenes sold under the trademark NEOPRENE and the chlorosulfonated polyethylenes sold under the trademark HYPALON (both products of Dupont) are examples of 10 commercially available chlorinated rubbers suitable for use in such adhesive formulations. The adhesive formulation will generally also contain one or 15 more curatives, crosslinkers, and/or accelerators (e.g., sulfur, peroxide, nitroso and oxime compounds), fillers, solvents (organic or water), pigments (e.g., carbon black), and the like.

One method of forming such rubber-to-metal composites is to bond a vulcanized rubber to an autodeposition coated metal object which has been sprayed with or dipped in the adhesive. Typically, the adhesive layer will be about 0.2 to about 3 mils thick. The coated metal object/adhesive/rubber assembly is subjected to heat (for example, temperatures between about 120°C and 200°C) and pressure (for example, about 50 to about 200 bar) in a mold wherein the adhesive cures and a bond between the coated metal object and the rubber is created. Alternatively, the rubber is not vulcanized prior to being attached to the metal object; both the rubber and the adhesive are then cured (vulcanized) in the heated mold.

EXAMPLE

A. Polymer Synthesis

A resin vessel equipped with a condenser is charged with a relatively low molecular weight diglycidyl ether of bisphenol A such as DER 331 (available from Dow Chemical), a flexibilizing epoxy resin such as CARDOLITE NC-514 (available from the Cardolite Corporation), and a chain extender such as bisphenol A and the contents heated to 120°C. A catalyst such as triphenylphosphine and a solvent such as toluene are charged to an addition tank and mixed until the catalyst is dissolved. The reaction is carried out under an atmosphere of inert gas at a temperature of 120°C to 150°C for 4 to 5 hours. Once the contents of the reactor reach 120°C, one-half of the catalyst solution in the addition tank is added to the reactor over

a period of 15 minutes. The contents of the reactor are allowed to react for approximately 1 hour. The reaction is exothermic. After 1 hour, the remainder of the catalyst solution is added over a period of 15 minutes. The reactor contents are held at 130°C to 150°C for an 5 additional 2 to 5 hours. Once the desired degree of reaction has been achieved (as measured, for example, by Weight Per Epoxide titration analysis), the reactor contents are cooled to 120°C. Additional solvent (e.g., methyl isobutyl ketone) is then added and the reactor contents allowed to cool to room temperature.

10 The amounts of the above-described components may be as shown in the following table.

15

20

	<u>Component</u>	<u>Wt., g</u>	<u>Wt. %</u>	<u>WPE¹</u>	<u>Epoxy Eq.</u>	<u>OH Eq.</u>
	Cardolite NC-514 Epoxy Resin	38.25	8.46	350	0.1093	
5	Bisphenol A Chain Extender	73.86	16.34			0.6470
	DER 331 Epoxy Resin (1 st Charge)	88.46	19.57	187	0.4730	0.0233
10	Toluene (1 st Charge)	5.62	1.24			
	Triphenyl Phosphine (catalyst)	0.39	0.09			
	DER 331 Epoxy Resin (2 nd Charge)	54.43	12.04	187	0.2911	0.0144
15	Toluene (2 nd charge)	7.16	1.58			
	Triphenyl Phosphine	0.50	0.11			
20	Methyl Isobutyl Ketone	183.29	40.55			
		_____	_____	_____	_____	_____
	Total	451.96	100		0.8734	0.6847

¹WPE = weight per epoxide

B. Processing of Polymer into Emulsion

25 A first reaction vessel equipped with a mixer is charged with deionized water and a surfactant such as RHODAPEX CO 436 (containing 58% of an ammonium salt of sulfonated nonylphenol ethoxylate) and the contents mixed slowly for 20 minutes or until homogeneous. A second reaction vessel equipped with a heavy-duty stirrer, heating and cooling means, and vacuum

distillation capability is charged with a solvent such as methyl isobutyl ketone under an inert gas atmosphere. After turning on the stirrer, the resin synthesized as described in A above, a cross-linker such as VESTAGON B1530, optionally, a coalescing solvent such as TEXANOL, and, optionally, 5 other additives (e.g., MODAFLOW 2100 levelling agent) are charged to the second reaction vessel. The resulting mixture is heated at approximately 35°C for about 1 hour until all the components are dissolved and the mixture is homogeneous.

10 The contents of the two reaction vessels are pumped, according to their proportions, through an in-line rotor stator emulsifier and into a holding tank to form a pre-emulsion. The pre-emulsion is then fed using a continuous duty 2 gallon/minutes 80 psi discharge feed pump into a MICROFLUIDIZER dispersing apparatus equipped with a heat exchanger (minimum 4 square feet exchange area) capable of cooling 8.8 liters/minute 15 below 35°C. The average particle size of the emulsion formed is preferably in the range of 150 to 250 nm. The emulsion is then pumped into a clean dry distillation vessel.

For distillation, the vessel can be filled to approximately 70% capacity. 20 The contents of the vessel are heated to 38°C ($\pm 2^\circ\text{C}$). The vacuum applied should be sufficient to keep the distillation rate approximately constant. The emulsion temperature should not exceed about 40°C. Distillation is continued until all of the solvent has been removed (with certain solvents such as methyl isobutyl ketone, an azeotrope with water will be removed).

A pigment dispersion such as AQUABLACK 255A carbon black in water is added to the stripped emulsion and mixed thoroughly until homogeneous.

The solids (non-volatiles) level is then adjusted to approximately 38% using deionized water. The resulting dispersion may be used as an autodeposition replenisher or, alternatively, as a component of the autodeposition bath composition described in C below.

The amounts of the above-described components may be as shown in the following table.

	<u>Component</u>	<u>Wt.,g</u>	<u>Wt.,%</u>
10	Polymer Solution (60% Non-Volatile) ¹	425.35	22.79
	VESTAGON B1530 Cross-Linker ²	45.00	2.41
	MODAFLOW 2100 Levelling Agent	15.00	0.80
	TEXANOL Coalescing Agent	34.80	1.86
	Methyl Isobutyl Ketone	330.00	17.68
15	RHODAPEX CO436 Surfactant	16.29	0.87
	Deionized Water	1,000.00	53.58
	Total	1,866.44	100

20 ¹The non-volatile (solids) component has a weight per epoxide of 1741 and an -OH equivalent weight of 372, thus providing 0.1465 epoxy equivalents and 0.6855 -OH equivalents.

25 ²Containing the equivalent of 15.25 wt% NCO, thus providing 0.1634 NCO equivalents.

C. Preparation of Autodeposition Bath Composition

Deionized water (450 g per 1000 g of the final bath composition) is added to a container so as to fill approximately one-half of the container.

AUTOPHORETIC 300 starter (available from Henkel Surface Technologies)

is then added in an amount corresponding to 50 g per 1000 g of the final bath composition and mixed thoroughly. An amount of the dispersion obtained as described in Section B above sufficient to provide a solids level of 6% in the final bath composition is then added while mixing thoroughly,
5 taking care not to generate foam. Finally, sufficient water is added to bring the volume of the bath composition up to the desired operating level.

D. Metal Panel Coating

Metal panels (e.g., cold rolled steel) are coated by placing said panels (which may desirably be pre-cleaned using standard cleaning methods known in the autodeposition art) in the autodeposition bath composition described in C above for about 90 seconds at a temperature of about 21 to 24 degrees C, after allowing the bath to equilibrate for 24 hours first. The redox value of the bath composition is maintained in the range of from 300 to 400 mV by addition of aqueous hydrogen peroxide or the like. Free fluoride ion activity is monitored using a LINEGUARD 101 meter and associated free fluoride sensitive electrode and maintained in the range of from 150 to 300 microamperes by addition of aqueous hydrofluoric acid or the like. Additional quantities of the dispersion obtained in C above are added as needed to maintain a solids level of 5.5 to 6.5 %. Following the
10 coating step, the panels are rinsed for 1 minute using a desired rinse solution (e.g., deionized water alone at ambient temperature or a 1.5 wt % solution of calcium nitrate in water at 50 degrees C) and then cured by baking in an
15 oven for up to about 1 hour at 185 degrees C, for example.

What is claimed is:

1. A metallic substrate having a coating adhered thereto, said coating being obtained by autodepositing a polymer comprised of moieties derived from at least one epoxy resin which is a glycidyl ether of a first polyhydric phenol and at least one flexibilizing epoxy resin on said metallic substrate and curing said polymer.
5
2. The metallic substrate of claim 1 wherein at least one flexibilizing epoxy resin is a glycidyl ether derived from cardanol.
10
3. The metallic substrate of claim 1 wherein the first polyhydric phenol is bisphenol A.
15
4. The metallic substrate of claim 1 wherein said polymer is obtained by contacting said epoxy resin and said flexibilizing epoxy resin with at least one chain extender containing at least two epoxy-reactive groups selected from hydroxyl, carboxylic acid, carboxylic acid anhydride, and combinations thereof for a time and at a temperature effective to form said polymer, wherein said chain extender is preferably a second polyhydric phenol, which may be the same as or different from the first polyhydric phenol.
20
5. The metallic substrate of claim 1 wherein said metallic substrate is comprised of iron.

6. The metallic substrate of claim 1 wherein said polymer is cured using a blocked isocyanate cross-linker.

7. A composite comprised of the metallic substrate of claim 1, a rubber, 5 and an adhesive bonding said metallic substrate to said rubber.

8. The composite of claim 7 wherein the rubber is selected from the group consisting of natural rubber, nitrile rubber, and combinations thereof.

10

9. The composite of claim 7 wherein the adhesive is comprised of at least one chlorinated polymer and at least one curative.

15

10. A method of making an aqueous dispersion suitable for use in forming an autodeposited surface coating, said method comprising

20

a) contacting at least one epoxy resin and at least one chain extender containing at least two epoxy-reactive groups selected from hydroxyl, carboxylic acid, carboxylic acid anhydride and combinations thereof for a time and at a temperature effective to accomplish reaction of said epoxy resin and chain extender to form a polymer having an increased molecular weight as compared to the epoxy resin;

b) emulsifying a solution of the polymer in an organic solvent with water in the presence of an emulsifier to form an organic solvent-containing

intermediate emulsion; and

- c) removing the organic solvent from the organic solvent-containing intermediate emulsion to form the aqueous dispersion.

5 11. The method of claim 10 wherein the emulsifier is an anionic surfactant.

12. The method of claim 10 wherein at least one epoxy resin is a glycidyl ether of a polyhydric phenol.

10

13. The method of claim 10 wherein at least one chain extender is a polyhydric phenol.

14. The method of claim 10 wherein the aqueous emulsion has an 15 average particle size in the range of from about 100 to about 300 nm.

15. The method of claim 10 wherein the organic solvent is removed in step (c) by azeotropic distillation.

20

16. The method of claim 10 wherein the organic solvent is removed in step (c) at a temperature less than about 50°C.

17. The method of claim 10 wherein step (a) is performed in the presence of the organic solvent.

5 18. The method of claim 10 wherein step (a) is performed in the presence of a catalyst.

10 19. The method of claim 10 wherein the organic solvent is selected from the group consisting of aromatic hydrocarbons, aliphatic ketones, and mixtures thereof.

10 20. The method of claim 10 wherein step (a) is performed at a temperature in the range of from about 100°C to about 200°C.

15 21. An aqueous emulsion comprised of water and a polymer containing moieties derived from at least one epoxy resin which is a glycidyl ether of a first polyhydric phenol and at least one flexibilizing epoxy resin.

20 22. The aqueous emulsion of claim 21 additionally comprising at least one anionic surfactant.

23. A metallic substrate having a coating adhered thereto, said coating being obtained by autodepositing a polymer comprised of moieties

derived from at least one epoxy resin which is a glycidyl ether of a polyhydric phenol and flexibilizing segments selected from the group consisting of polymethylenes, polyesters, polyoxyalkylenes, and combinations thereof.